FEMTOSECOND PHOTOIONIZATION STUDIES OF ACETYL UNIMOLECULAR DECOMPOSITION

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ABSTRACT

Femtosecond photoionization spectroscopy has been used to measure unimolecular decay rates for acetyl produced by photodissociation of acetic acid and acetyl cyanide near 200 nm. Acetyl precursors with simple (diatomic) accompanying fragments and well characterized product energy distributions, such as for these precursors, permit quantitative investigation of the dissociation dynamics. Agreement between the observed lifetimes and RRKM lifetimes at the average internal energy is poor, especially for acetic acid. But the agreement is greatly improved when the energy distribution (the shape of the distribution) of the acetyl is properly taken into account. In addition, *ab initio* calculations have been used to determine that the acetyl cyanide absorption band at 195 nm is a due to a π-π^* transition.

INTRODUCTION

- Acetyl (CH_3CO): an intermediate in numerous photodissociation studies involving multiple dissociations:
  - energy partitioning (primary → acetyl internal energy → secondary)
  - unimolecular dissociation dynamics (rates, product yields and energies)

- There is continuing interest in understanding when and why molecules exhibit “non-RRKM” or nonstatistical behavior; *e.g.,* when IVR is slow compared to dissociation

- Investigating acetyl dissociation dynamics for various precursors and internal energies explores state-specific (extrinsic non-RRKM) effects

- It is now possible to directly measure dissociation times on the time scale that IVR occurs for moderately to highly excited molecules:
  ultrafast and product studies of photodissociation are complementary

ACETYL RADICAL UNIMOLECULAR DISSOCIATION DYNAMICS

- The acetyl dissociation barrier is well determined (17±1 kcal/mole)[1,2]
- Acetyl from various *precursors* exhibits nonstatistical dissociation behavior
  - *Acid Halides*:
    - measuring parent translational energy distribution establishes acetyl internal energy[1,3,4]
    - acetyl from acetyl chloride: dissociates slower than RRKM predicts[4]
    - acetyl dissociation product energies are better fit by Sudden Adiabatic Impulse model than by a statistical model[5]
  - *Acetone*:
    - polyatomic fragaments - complicate determining (acetyl) internal energy
    - acetyl with both high[6] and low internal[4,7] energy dissociates more slowly than RRKM predicts
    - lifetime observed for acetyl (~3.1 ps for h_3)[7a] from acetone at 193 nm:
      - longer than predicted by RRKM calculations (~1 ps) using the best estimates available for acetyl internal energy
      - isotope dependence less than RRKM predicts[7b]

PHOTODISSOCIATION OF ACETYL CYANIDE AND ACETIC ACID

- Acetyl precursors with well characterized partner fragment energies: better assessment of the RRKM behavior of secondary acetyl decomposition based on directly measured dissociation times

- Acetyl via photodissociation of acetic acid and acetyl cyanide:
  - determination of the internal energies for the relatively simple diatomic fragments is spectroscopically feasible
  - the product energies have been recently measured in photodissociation studies near 200 nm[8,9]

- Ultrafast deep UV, mass-resolved MPI used to measure parent and acetyl dissociation times: compare with results from previous product studies

- *Ab initio* calcuations and VUV absorption spectra for acetyl cyanide used to identify the 193 nm transition for acetyl cyanide

BACKGROUND AND PREVIOUS STUDIES

Acetyl Cyanide at 193 nm

(Horwitz et al.[8a] and North et al.[8b])

- Major (if not exclusive) primary dissociation channel: to acetyl and cyanide

$$CH_3COCN \rightarrow CH_3CO + CN$$

- Nearly complete secondary acetyl dissociation
- Negligible product angular anisotropy[8b]
- Product energy distributions measured
  - CN internal state distributions (R and V) measured spectroscopically
  - Photofragment translation energies distributions measured for CN
  - *The acetyl internal energy distribution determined by difference from* E_{avl}
- Unresolved issues: dissociation energy is not precisely known, assignment of 193 nm transition, explanation of isotropic products

ACETIC ACID PHOTODISSOCIATION

(Guest and coworkers[9a,b])

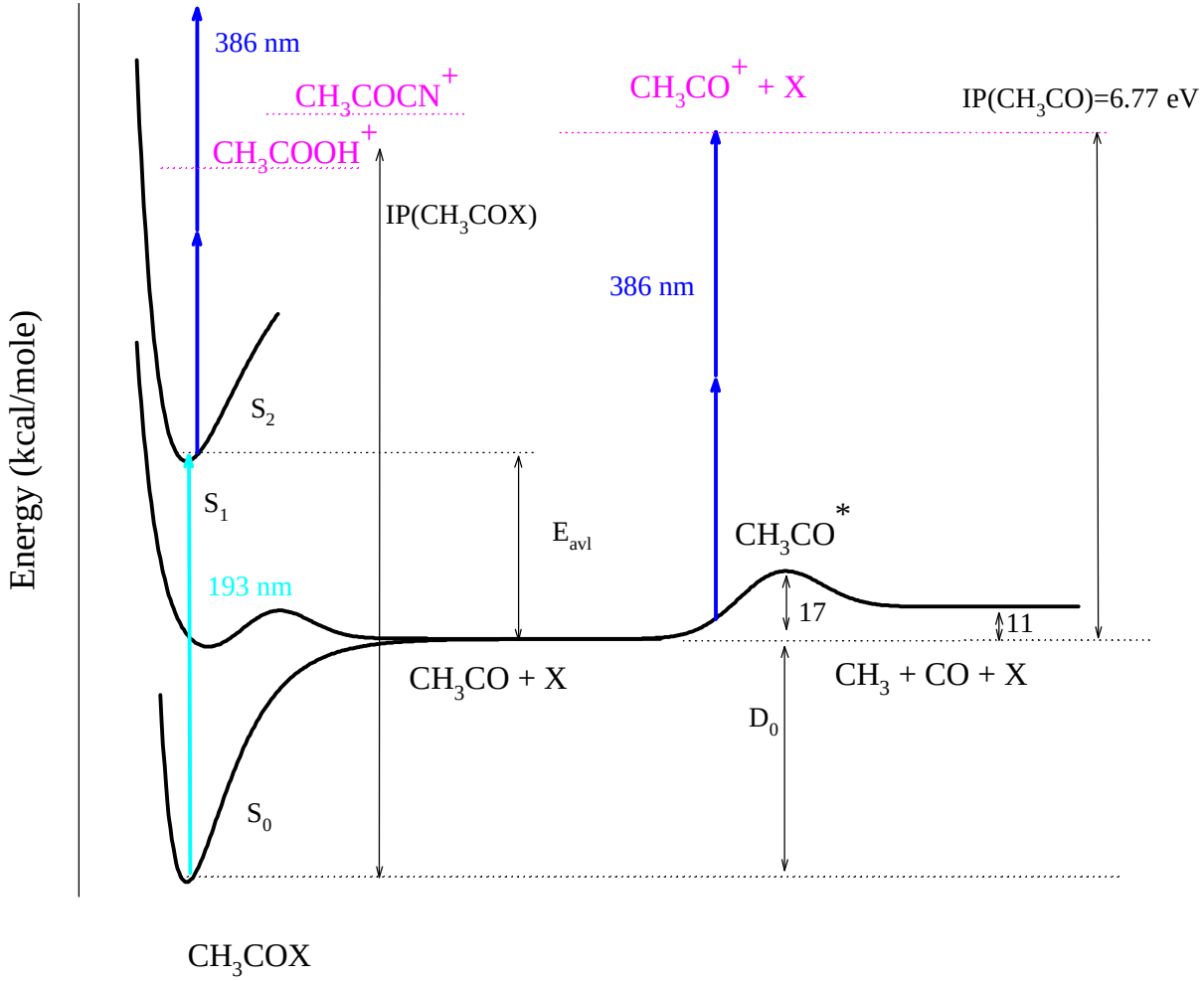
- Studies for excitation at 218 nm[9a,b] and 200 nm[9c]
- Primary dissociation channel: to acetyl and hydroxyl radicals

$$CH_3COOH \rightarrow CH_3CO + OH$$

- Negligible product angular anisotropy (n-π* transition)
- OH internal state distributions (R and V) measured spectroscopically

  results for OD not consistent with impulsive partitioning[9b]
- Doppler measurement of OH translation energy
  - Similar (~14 kcal/mole) for both excitation energies
  - Exit barrier suggested (also similar to other carbonyls: acetone S_1)
- *The average acetyl internal energy is determined for 200 nm excitation*

Schematic Potential Energy Surface



ENERGETICS AND PRODUCT ENERGY DISTRIBUTIONS FOR PHOTODISSOCIATION OF ACETYL CYANIDE AND ACETIC ACID[a]

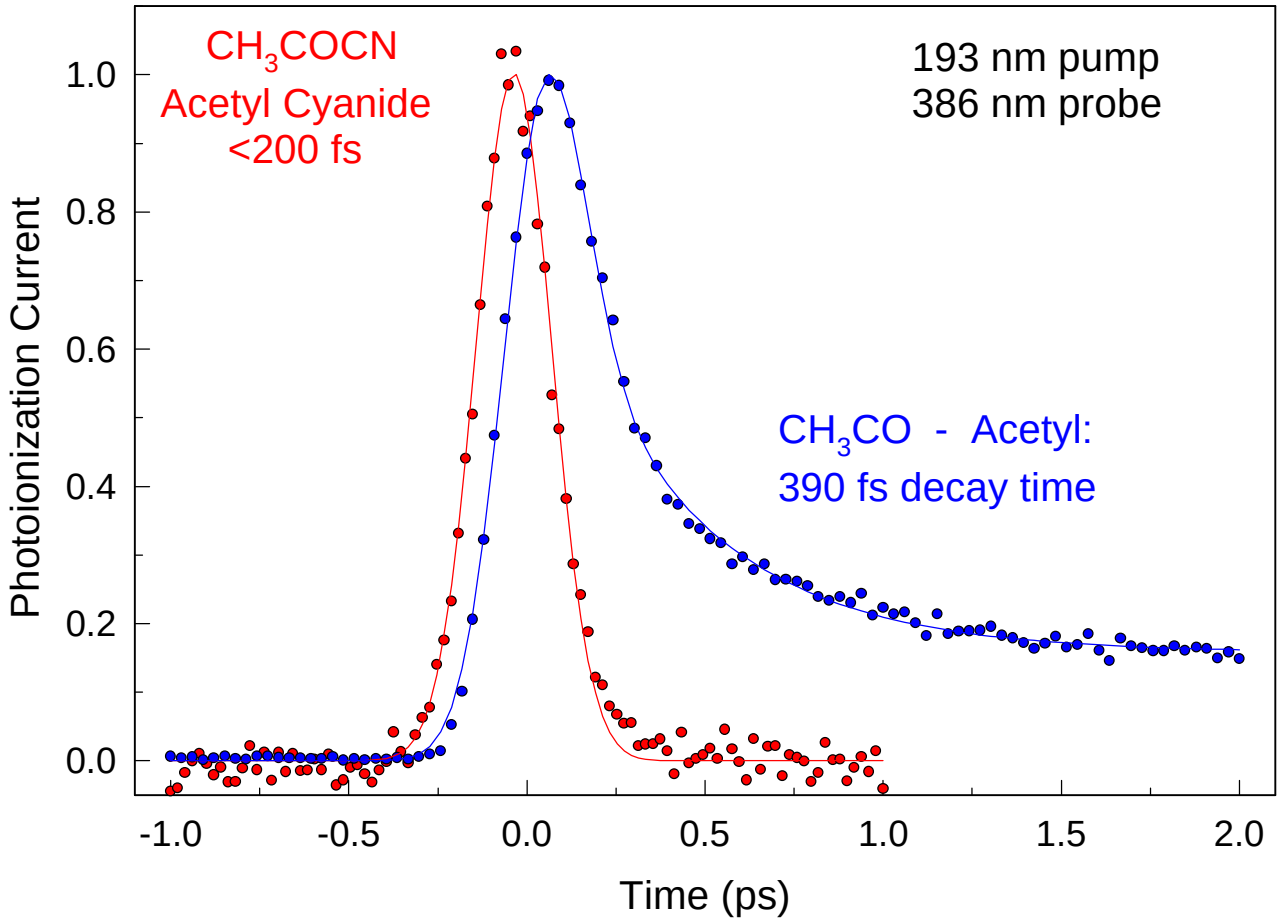
λ_{exc}(nm,kcal/mole))	E_{avl}	$<E_t>$	$<E_r(X)>$	$<E_v(X)>$	$<E_{int}(CH_3CO)>$[b]
CH_3COOH (X=OH), D_o=110					
218 (131.2)	21.2	13.7	1.2	<0.2	4.9
200 (143.0)	33.0	14.5	1.4	<0.4	16.7
194 (147.7)	37.7	15.0[c]	1.4[c]	<0.5[c]	20.8
CH_3COCN (X=CN), D_o=102.2					
193 (148.1)	45.9	7.2	3.6	1.2	33.9

a. Energies in kcal/mole

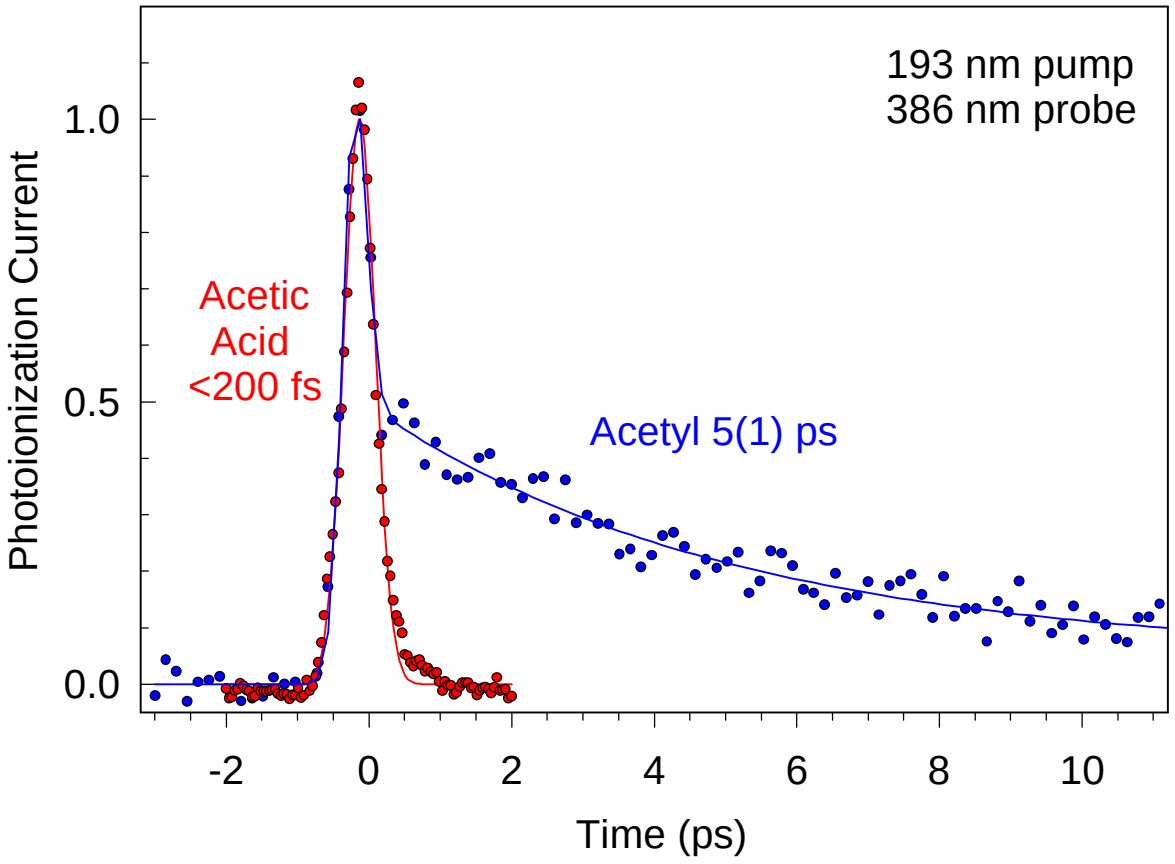
b. Obtained by difference

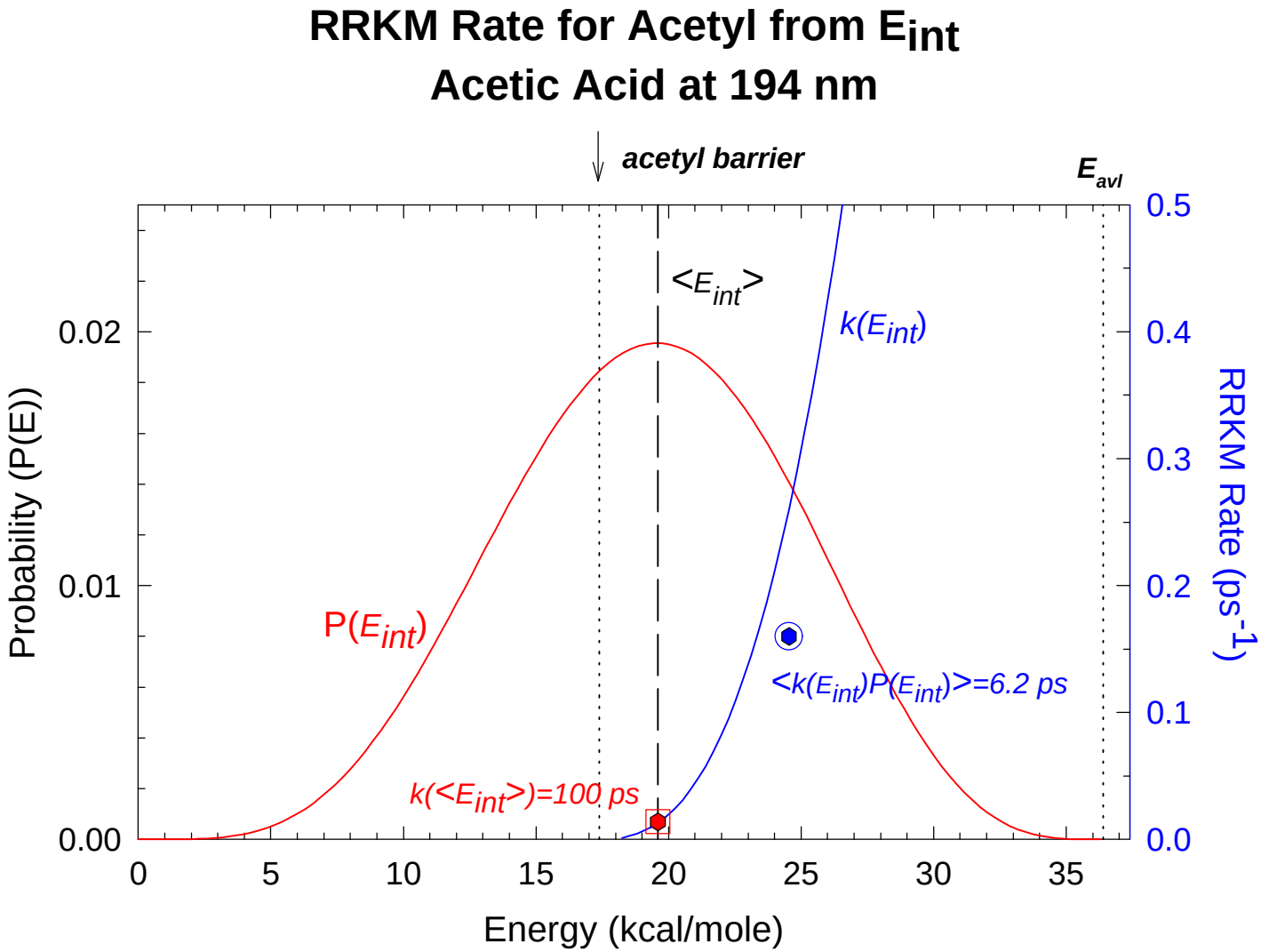
c. Extrapolated from measured values at 200 nm

Photodissociation of Acetyl Cyanide and Secondary Acetyl Decomposition



Photodissociation of Acetic Acid and Secondary Acetyl Decomposition




RRKM Rate for Acetyl from E_int
Acetic Acid at 194 nm
acetyl barrier
E_avl
<E_int>
k(E_int)
P(E_int)
<k(E_int)P(E_int)>=6.2 ps
k(<E_int>)=100 ps
Probability (P(E))
RRKM Rate (ps^-1)
Energy (kcal/mole)
0.00
0.01
0.02
0.0
0.1
0.2
0.3
0.4
0.5
0
5
10
15
20
25
30
35

RRKM LIFETIMES[a] AND $\langle E_{int} \rangle$

λ_p(nm)	$\langle E_{int} \rangle$ (kcal/mole)	Precursor	$\tau_{\langle Eint \rangle}$	τ_{dist}	τ_{obs}
194.5	19.6	CH_3COOH	100.	6.2	5 (1)
194.5	31.0[b]	CH_3COCN	0.74	0.56	0.56
194.0	31.4[b]	CH_3COCN	0.70	0.53	0.52
193.5	31.7[b]	CH_3COCN	0.63	0.50	0.46
193.0	32.1[b]	CH_3COCN	0.60	0.47	0.39

a. RRKM lifetimes were calculated using the UNIMOL program suite[10a] and vibrational frequencies reported by Deshmukh et al.[10b]
b. Assumes a dissociation energy of 102.25 kcal/mole for acetyl cyanide.

CONCLUSIONS FROM ULTRAFAST STUDIES

- For both molecules, the parent excited state is short-lived (<300 fs) and dissociates to form acetyl

- Agreement between observed and predicted RRKM acetyl lifetimes:
  - Poor agreement with rate for *average* internal energy: $k^{RRKM}(\langle E_{int} \rangle)$
  - Good agreement with rate estimated using $k(E_{int})$ and $P(E_{int}$ (acetyl))
  - $k^{RRKM}(\langle E_{int} \rangle)$ $\langle k^{RRKM}(E_{int}) \rangle$ and $\langle k^{RRKM}(E_{int}) \rangle$ k^{obs}

- This approach will not yield better agreement between data for acetyl from acetone and RRKM model since the observed lifetime is already longer

- HOW is acetyl is prepared?
  - For acetone at 193 nm: predissociation from a Rydberg state
  - For acetic acid at 200 and 218 nm: from excitation of a π^* n transition
  - For acetyl cyanide at 193 nm: *NOT* well determined, may be from excitation of a π^* π transition

ISSUES FROM FEMTOSECOND STUDIES - Mostly *Unresolved*

- *Ionization Potential of Acetyl Cyanide:*
  - Using 193 nm pump/257 nm (THG) probe, no acetyl cyanide parent ions observed
  - This suggests: *vertical* IP 11.2 eV (Acetone ions observed this way, IP = 9.7 eV)

- *Product Anisotropy and Excited State Lifetime:*
  - North et al.[8b] found nearly zero anisotropy (β 0) for dissociation of acetyl cyanide
  - If the transition were n→3*s*, they thought β 1.25;
  - Low anisotropy attributed to a long lived excited state and rotational averaging:
    does not agree with our measured lifetimes

- *Assignment of acetyl cyanide transition at 193 nm*
  - Rydberg state energy levels correlate with IP so that the 193 nm transition in acetyl cyanide is not n→3*s*, contrary to the assignment by North et al.[8b]
  - What is the transition? Does its' transition moment direction explain the anisotropy?

- Acetyl Cyanide Dissociation Energy - less unresolved

  Dissociation energy used as adjustable parameter to fit both the internal energy distributions derived by North et al.[8b] and our lifetime data
  - D_o(best) = 102.2 kcal/mole
  - Within 0.25 kcal/mole of D_o used by of North et al.[8b]; within 2.25 kcal/mole of recent calculation[11a]; within 2.5 kcal/mole of the NIST value[11b] (which is ±2.5kcal/mole)

CN SUBSTITUTION INCREASES IONIZATION POTENTIAL

Molecule	OH	CN
CH_3X	10.84	12.2
CH_3CH_2X	10.48	11.85
CH_3COX	10.65	(11.18-11.26)

- Estimate Rydberg state energy with Rydberg formula and IP = 11.22eV:

$$E_{n,\,l} = IP - (13.606/(n - \delta_l)^2)$$

where δ_l 1 for *s*, 0.6 for *p*, and 0.1 for *d*.

- For the 3s n transition of acetyl cyanide, $E_{n,\,l}$ = 7.82 eV (158 nm)
  For acetone 3s, calculation agrees with observed: 6.30 eV (197 nm)
- 194 nm transition in acetyl cyanide **is not** to a Rydberg state.

VUV SPECTRA AND EXCITED STATE CALCULATIONS FOR ACETYL CYANIDE

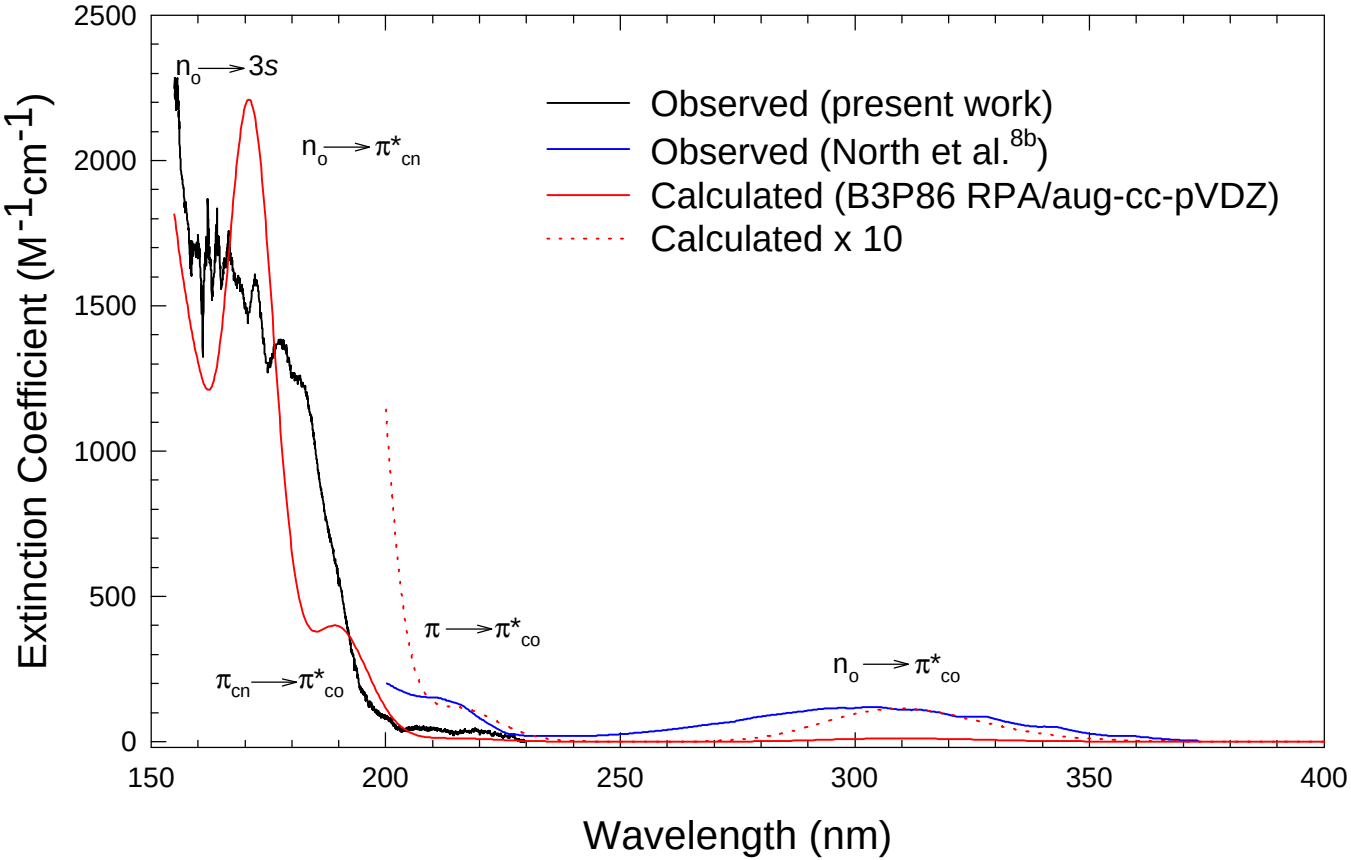
194 nm Transition Assignment for Acetyl Cyanide

- Gaussian 94 calculations using various methods:
  - CI Singles demonstated to accurately calculate excited states of alkenes.
  - CIS applied to carbonyl containing species yields disappointing results: no substantial improvement with larger basis set or level of calculation

- Wiberg et al.[12] used Time Dependent Density Functional methods to calculate the excited states of acetone, formaldehyde, and acetaldehyde with encouraging results: typically within 0.2 eV of experimental values.

- G98 supports these calculations
  - Carried out for both acetone and acetyl cyanide
  - Structures optimized at the MP2 level and the B3P86 functional was used (as done by Wiberg[12])
  - Results for acetone with large basis sets in good agreement with observed spectra including intensities: similar accuracy expected for acetyl cyanide

Calculated and Experimental Acetyl Cyanide Absorption Spectrum



CONCLUSIONS FROM CALCULATIONS

- The 193 nm absorption is due to a π^* π rather than 3s n transition
  - Indicated by orbitals
  - The 3*s* Rydberg state is calculated to be at 7.57 eV

- Assignment consistent with higher energy location of Rydberg and IP
  - G94 calculation at MP2 level: IP(adiabatic) = 11.49 eV
  - Measured by McElvany and Baronavaski,[13] FTMS bracketing experiments: IP(adiabatic) = 11.22±0.04 eV
  - Consistent with effect of CN addition on hydrocarbon IP's
  - Explains why we did not see parent ions with FHG+THG

- The transition moment for the 194 nm band is at an angle of 57 with respect to the CN bond
  - Results in β = -0.11, probably too small for North et al.[8b] to measure
  - Long parent lifetime not required to explain isotropic products

- The calculated spectrum, using a band width of ~4000 cm^{-1}, is in good agreement with our experimental spectrum. A better VUV spectrum is required for a more detailed assignment.

CONCLUSIONS

- Theory in nearly quantitative agreement with experimental data for excited states, even for molecules with heteroatoms

- The data on Acetyl Cyanide are consistent
  - Short (<300 fs) parent excited state lifetime
  - Acetyl dissociation rate consistent with RRKM model, provided that rate dependence of energy and acetyl internal energy distribution considered
  - 194 nm transition: π^* π rather than to 3s Rydberg state
    - accounts for isotropic products: transition moment close to magic angle relative to CN bond direction
    - correlates with IP, which is significantly higher (>1 eV) than acetone

- Acetyl from acetic acid and acetyl cyanide excited near 200 nm seems to exhibit RRKM behavior
  - Detailed comparison possible for precursors with simple companion fragments and for which product energy measurements are available
  - Dynamics appear nonstatistical for other precursors
  - Implies state-specific, preparation-dependent behavior (extrinsic non-RRKM)

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